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A vegetation control on seasonal variations in global atmospheric mercury

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Abstract

Anthropogenic mercury emissions are transported through the atmosphere as gaseous elemental mercury (Hg(0)) prior to deposition to Earth's surface. Strong seasonality in atmospheric Hg(0) concentrations in the Northern Hemisphere has been explained by two factors: anthropogenic Hg(0) emissions are thought to peak in winter due to higher energy consumption, and atmospheric oxidation rates of Hg(0) are faster in summer. Oxidation-driven Hg(0) seasonality should be equally pronounced in the Southern Hemisphere, which is inconsistent with observations of constant year-round Hg(0) levels. Here, we assess the role of Hg(0) uptake by vegetation as an alternative mechanism for driving Hg(0) seasonality. We find that at terrestrial sites in the Northern Hemisphere, Hg(0) co-varies with CO_2, which is known to exhibit a minimum in summer when CO_2 is assimilated by vegetation. The amplitude of seasonal oscillations in atmospheric Hg(0) concentration increases with latitude and is larger at inland terrestrial sites than at coastal sites. Using satellite data, we find that the photosynthetic activity of vegetation correlates with Hg(0) levels at individual sites and across continents. We suggest that terrestrial vegetation acts as a global Hg(0) pump, which can contribute to seasonal variations of atmospheric Hg(0), and that decreasing Hg(0) levels in the Northern Hemisphere over the past 20 years can be partly attributed to increased terrestrial net primary production.

Gaseous elemental mercury (Hg(0)) is the dominant form of natural and anthropogenic Hg emissions and is transported globally through the atmosphere.[1] Hg deposition to earth surfaces occurs either by direct Hg(0) dry deposition or after oxidation to reactive Hg(II), which is scavenged from the atmosphere by wet and dry deposition.[2] In addition to primary anthropogenic emissions, Hg is also re-emitted as Hg(0) from land and ocean surfaces to the atmosphere after reduction of Hg(II) pools in terrestrial and aquatic ecosystems.[2]

The short-term balance between Hg emission, deposition and re-emission processes governs diurnal and seasonal Hg(0) variations. For example, strong seasonal variations in atmospheric Hg(0) concentration have been described for most background sites in the temperate Northern Hemisphere (NH) with peaks in winter and minima in summer.[3-6] Two hypotheses for the observed Hg(0) seasonality are commonly proposed. The first hypothesis assumes that Hg(0) variations are directly related to primary anthropogenic Hg(0) emissions from coal combustion which are thought to be higher in winter due to higher energy demands for heating.[3,5] Global Hg models have not yet been able to test this hypothesis, as current anthropogenic Hg emission inventories have no seasonal resolution and are kept constant throughout the year in models.[7-9] The second hypothesis suggests that atmospheric Hg(0) oscillations are due to variations in atmospheric Hg(0) oxidation rate and subsequent Hg(II) deposition, which are both highest in summer in global Hg models.[7-10] Models incorporating atmospheric Hg(0) oxidation simulate equally pronounced (amplitudes of approx. 18%) seasonal Hg(0) variations in both Hemispheres. Hg(0) measurements at temperate sites in the Southern Hemisphere (SH), however, are constant with no seasonal oscillations.[6,11] Conversely, methane concentrations in the SH, for which atmospheric oxidation by OH radicals represents the most important sink, do show strong seasonal variations.[12] The absence of Hg(0) seasonality in the SH questions the dominant role of atmospheric Hg(0) oxidation.

Foliar uptake of atmospheric Hg(0) has long been recognized as a potentially inportant pathway for atmospheric Hg deposition.[13,14] The magnitude of terrestrial-atmosphere net Hg(0) exchange (foliar Hg(0) uptake - Hg(0) re-emission) however has been debated with studies suggesting a net emission of Hg(0)[15-18] and others suggesting net Hg(0) deposition.[19] A recent review of Hg(0) flux measurements over terrestrial surfaces concludes that there is no consensus whether terrestrial ecosystems are a net sink or source for Hg(0) (-513 to 1651 Mg a^{-1}, 25 to 75 percentile).[20] Most Hg(0) flux studies however focused on soil re-emission, and thus neglected foliar Hg(0) exchange.[20]

There are several lines of evidence for net Hg(0) deposition to terrestrial ecosystems that all invoke direct vegetation uptake of atmospheric Hg(0). First, foliage tissue Hg concentrations increase continously over the growing season, implying that Hg(0) is taken up by vegetation through gas exchange and sequestered in leaf tissue.[14,21] Structurally incorporated Hg in leaf tissue derived from atmospheric Hg(0) therefore likely has a lower re-emission potential due to photo-reduction,[21,22] compared to Hg(II) deposited onto external leaf surfaces.[23] Second, global litterfall Hg deposition to soils - representing Hg(0) net uptake by foliage - is estimated to be 1000-1200 Mg yr^{-1} [17,24] representing half of primary anthropogenic emissions.[25] Third, vegetation and soil Hg stable isotope signatures, which discern foliar Hg(0) uptake from Hg(II) wet deposition, put firm constraints on vegetation Hg(0) uptake dominating (50-80%) Hg net deposition at terrestrial sites.[22,26-28]

Here, we investigate the role of vegetation Hg(0) uptake in modulating global atmospheric Hg(0) distribution and seasonality. We compare the atmospheric dynamics of Hg(0) with those of CO_2 - a tracer for gas exchange by vegetation - for which seasonal oscillations in the Northern Hemisphere (NH) are attributed to the balance of CO_2 assimilation and respiration during the year.[29-31]

Correlation of Hg(0) and CO_2 seasonality

We investigated multi-year time series of Hg(0) and CO_2 at seven NH and SH background sites (mean Hg(0) < 2 ng/m^3) and Hg(0) at an additional 43 global sites. Multi-year Hg(0) and CO_2 observations of the five NH background sites, normalized for linear long-term trends, show seasonal variations with highest concentrations in winter and minima in summer and fall (**Fig. 1, S1, S3, S5 and S6**). For all NH sites including both of inland and coastal sites, we found a significant positive correlation between multi-year averages of monthly Hg(0) and CO_2 concentrations normalized for long-term trends (Birkenes, Norway (R^2= 0.53, p=0.003), Schauinsland, Germany (R^2= 0.40, p=0.012), Mace Head, Ireland (R^2= 0.70, p<0.001), Pallas, Finland (R^2= 0.45, p=0.007) and Egbert, Canada (R^2= 0.76, p<0.001), **Fig. S2**). In the SH, the available data are from two coastal sites, Cape Point (South Africa) and Amsterdam Island (France), with the latter surrounded by 3000 km of ocean. Both SH sites show small day-to-day variability, small diurnal variation, small seasonal amplitudes in CO_2 (<3 ppm, <1%) and Hg(0) (<0.1 ng/m^3, <10%) (**Fig. 1**) and no significant correlation between the two trace gases (**Fig. S2**). This suggests low anthropogenic contributions (i.e., no pollution plumes) resulting in Hg(0) distribution that is relatively constant throughout the day and seasons.

Two thirds of the primary anthropogenic emissions are to the NH,[32] which is the main explanation for the large interhemispheric gradient in Hg(0) concentrations.[6] We find that the interhemispheric gradient ($\Delta Hg_{45°N-45°S}$) is largest in February (0.68 ng/m^3) and smallest in September (0.36 ng/m^3) with a yearly average of 0.52 ng/m^3 (**Fig 2A**). Yet seasonal amplitudes of Hg(0) measurements at temperate NH background sites are much larger than in the SH, averaging 0.39 ng/m^3 (equivalent to 25% of the average annual Hg(0) concentration of 1.5-1.7 ng/m^3),[6] and were 6 times larger than the corresponding CO_2 amplitudes (4%). Excluding Polar sites (see below), we find a positive correlation (R^2=0.78, p<0.01) between seasonal Hg(0) (Sep-Feb) and CO_2 (Aug-Feb) amplitudes (**Fig. 2C**). Amplitudes of seasonal CO_2 oscillations are largest at high NH latitudes and decrease towards the south with minimal oscillations in the SH, which has been related to smaller land masses in the SH and ecosystems serving as net sinks in summer and net sources in winter.[29-31] We find a significant correlation between the seasonal Hg(0) amplitudes of all background sites (n=38) and latitude (R^2 = 0.42, p<0.001, **Fig. 2B**). However, Hg(0) amplitudes are confounded by additional factors. For example, we explain the lower amplitude at Egbert (Ca) by relatively high contributions of polluted air masses throughout the year (**Fig. S12**). Comparing all investigated sites, we find significantly higher Hg(0) amplitudes at inland background sites compared to coastal sites, both for Europe (0.39 ng/m^3 vs. 0.25 ng/m^3, n=13, p<0.05, 2-sided t-test) and North America (0.41 ng/m^3 vs. 0.27 ng/m^3, n=18, p<0.05, 2-sided t-test). A special case is a different seasonality of Hg(0) in the Arctic, which is characterized by well-documented spring minima due to sea-salt induced atmospheric mercury depletion events (AMDEs) and an unusual summertime maximum.[33] Observations from SH terrestrial background sites are few, yet the first data from Bariloche, Patagonia (Ar) revealed seasonal Hg(0) oscillations with minima in SH summer and autumn.[34]

If seasonal variations in atmospheric Hg(0) were mainly due to oxidation rates and ocean re-emission,[7-9] we would expect higher Hg(0) amplitudes at coastal sites and in the SH, which is contrary to the patterns described above. The fact that the highest seasonal amplitudes are observed at inland terrestrial background sites — along with similar patterns observed for CO_2 — is consistent with an important role of vegetation Hg(0) uptake in modulating global atmospheric Hg(0) concentrations. Individual ecosystem-scale studies have reported enhanced Hg deposition fluxes during vegetation growth periods[22,35] resulting in lower local atmospheric Hg(0) levels over vegetated surfaces.[27,36,37] The NH is not only more populated but also has a much larger land mass (39% land) compared to the SH (19%

land), resulting in higher vegetation Hg(0) uptake which may explain the weaker interhemispheric gradient during the NH growing season.

Most NH sites reveal a notable 1-month offset in Hg(0) summertime minima (Sep) compared to CO_2 (Aug) (**Fig. S3, S6**). Diurnal patterns between Hg(0) and CO_2 are anti-correlated during summer, but not in winter (**Fig. S4; See SI for details**). Differences in diurnal oscillations (**Fig. S4**) and later seasonal minima of Hg(0) relative to CO_2 suggest that Hg(0) uptake by vegetation continues during periods of net CO_2 respiration (i.e., nighttime and fall) when CO_2 ecosystem exchange turns from net assimilation (sink) to net respiration (source).[38] It is interesting to note that Hg(0) hence follows a similar behavior as carbonyl sulfide (COS), a tracer for stomata conductance of vegetation, for which seasonal patterns are strongly related to CO_2 but diurnal variations are decoupled from CO_2.[39,40] This suggests that vegetation Hg(0) uptake is controlled by gas exchange as approximated by CO_2 here. Net ecosystem CO_2 respiration however does not result in corresponding losses of Hg(0), which is supported by flux measurements at individual sites.[35] Observed Hg(0) concentration minima in September may be further amplified by a shallower planetary boundary layer (PBL) in autumn leading to a reduced mixing of surface air with global background air.[31]

Variations in Hg(0) vs. vegetation activity

We compared multi-year averages of monthly Hg(0) concentrations with the satellite-based Normalized Differenced Vegetation Index (NDVI), representing the vegetation photosynthetic activity at the location of the 44 NH monitoring sites (0.1° resolution). We find a significant correlations between monthly Hg(0) concentrations and NDVI for 22 of the 44 investigated sites. For the NH background sites with corresponding Hg(0) and CO_2 data, NDVI significantly correlated with both trace gases (**Fig. 3**), with the exception of Hg(0) at one site (Schauinsland, De). For example, at Pallas, Fi NDVI was able to explain 69 % and 82% of seasonal Hg(0) and CO_2 variation, respectively. The correlations between Hg(0) and NDVI were strongest at background sites in Canada ($R^2 > 0.75$ for e.g. Burnt Island, or Kejimkijuk, **Fig. S8**, Table S2), Scandinavia ($R^2 > 0.6$ for e.g. Andoya, Bredkäle, or Vavihill, **Fig. S9**, Table S3) as well as for Mountain sites in China ($R^2 \approx 0.5$ for e.g. Mt. Damai, Mt. Leigong, Mt. Chanbai, **Fig. S10**, Table S4). For urban sites in North America (e.g. Salt Lake City, Houston or Detroit, **Fig. S7**, Table S2) or Asia (Beijing, Nanjing, **Fig. S10**, Table S4) we did not find a significant correlation between Hg(0) and NDVI, suggesting that local anthropogenic emissions dominates Hg(0) levels at these urban sites. The strong correlations between Hg(0) and NDVI at most background sites further support the notion that vegetation uptake is responsible for Hg(0)

depletion in summer months when the vegetation activity is highest (high NDVI). We therefore suggest that NDVI satellite data might be a robust parameter to estimate terrestrial Hg(0) uptake on spatial and temporal scales, yet field studies directly comparing Hg(0) fluxes with vegetation cover are needed in order to validate this approach. A recent study found a strong correlation of soil Hg pools with NDVI across western North America,[41] suggesting a long-term control of vegetation Hg(0) uptake on soil Hg accumulation and sequestration, which also is supported by Hg stable isotope data.[22,26-28]

Seasonality of anthropogenic Hg(0) emission

Coal combustion represents a major primary Hg(0) emission source to the atmosphere.[32] We estimated the seasonal variation of anthropogenic Hg emissions (Table S5) by using monthly coal consumption data reported for the United States, Europe (EU27) and China. The estimates show a peak in Hg emission during the cold winter months attributed to increased energy consumption for heating (**Fig. 4**). In North America, there is a second peak in coal consumption and thus Hg(0) emission during hot summer months that exceeds the winter peak and is attributed to high energy consumption for air-conditioning of buildings.[42] Hg(0) concentrations measured at three urban monitoring sites in North America (Salt Lake City, Houston and Detroit)[43,44] closely follow these seasonal emission estimates, including a noticeable summertime Hg(0) increase (**Fig. 4**). Regional background sites in North America, however, show consistent summertime minima (**Fig. 4**), which cannot be explained by anthropogenic Hg emissions, implying that other processes drive the lower Hg(0) levels in summer. Inverse modeling that optimized terrestrial-atmosphere Hg(0) exchange fluxes to fit observational Hg(0) data, suggested enhanced summertime net Hg(0) deposition over eastern North America[45] supporting the strong role of vegetation Hg(0) uptake. In Europe and Asia, the anthropogenic Hg(0) emission estimates based on coal consumption data are highest in winter (Table S4) with no summertime increase and a seasonality similar to Hg(0) observations (**Fig. 4**). For the Waldhof site in central Europe, regional models have found a strong correlation between emission and particulate mercury but not for Hg(0).[46] We therefore conclude that variations in primary anthropogenic emissions alone cannot explain the observed seasonal Hg(0) variation in the NH.

Implications for global Hg cycling

Hg(0) concentrations measured in the PBL at terrestrial background sites reflect both deposition and emission processes. Therefore observed Hg(0) oscillations must be considered

as variations in net exchange (natural and anthropogenic emissions, vegetation uptake, and soil/vegetation re-emission). Strong depletion of atmospheric Hg(0) observed at terrestrial background sites in summer, despite highest solar radiation and therefore potential photo-reductive re-emission, suggests that terrestrial ecosystems serve as net sinks for Hg(0). A dominant role of vegetation Hg(0) uptake over other terrestrial emission and deposition processes also reconciles terrestrial Hg isotope constraints, which suggest 50-80% of vegetation and soil Hg to derive from plant Hg(0) uptake.[22,26-28] Considering the 20% amplitude of seasonal Hg(0) oscillations and an atmospheric Hg(0) pool of 4800 Mg,[47] we estimate that net Hg(0) sequestration is on the order of 1000 Mg a^{-1} of Hg(0) during the vegetation period, which is in agreement with foliage/litterfall estimates of 1000-1200 Mg a^{-1}.[17,24] The gross foliar Hg(0) uptake flux is likely larger. This suggests that at least half of the annual primary anthropogenic emissions are assimilated by terrestrial vegetation, where it is efficiently retained against re-emission to the atmosphere, though susceptible to transfer via soils to continental and coastal aquatic ecosystems.[22] We suggest that the vegetation pump controls to a large extent diurnal and seasonal cycling of atmospheric Hg(0) in the terrestrial PBL, which has large implications for global Hg cycling and interpreting and forecasting long-term trends. The absence of Hg(0) seasonality observed in the SH seems inconsistent with our current understanding of atmospheric Hg redox dynamics.[7,9,47] An important role of vegetation Hg(0) uptake on NH Hg(0) seasonality may imply that atmospheric Hg(0) oxidation is less significant than currently assumed.

Average Hg(0) levels in the NH have decreased by 20-40 % between 1990 and 2010, which was recently attributed to a cumulative 30% (≈600 Mg a^{-1}) decrease in global primary anthropogenic Hg(0) emissions.[25] Over the same time period, net primary production (NPP) is thought to have increased in the NH by 0.13-0.15 Pg C a^{-1}.[48,49] Assuming median foliar Hg concentrations of 24 ng g^{-1},[17] we estimate that Hg(0) deposition by NH vegetation uptake today has increased by ≈140 Mg a^{-1} relative to 1990. We therefore suggest that a significant fraction of the observed decrease in NH atmospheric Hg(0) concentrations can be attributed to increased vegetation uptake of Hg(0). Recent estimates of gross primary production (GPP), based on atmospheric COS cycling, suggested even larger increases in GPP by 31% during the twentieth century,[50] that may have strongly counterbalanced estimated increases in Hg(0) emissions. Regional reductions in vegetation cover by deforestation[51] or droughts[49], on the other hand, would weaken the vegetation Hg(0) pump and result in higher atmospheric Hg(0) concentrations. We therefore emphasize the need to incorporate seasonal and spatial variability in vegetation uptake of Hg(0) into global Hg models. In addition, trends in

vegetation activity should be incorporated in models reconstructing past and predicting future Hg(0) levels. The effects of Hg(0) uptake by vegetation related to climate change and land-use change should be considered when discussing mitigation strategies to reduce human Hg exposure. Finally, the paradigm shift we propose regarding the importance of vegetation Hg(0) uptake as a Hg deposition pathway demands revised Hg deposition monitoring strategies by environmental agencies.

FIGURE CAPTIONS

Fig. 1: Time records of atmospheric Hg(0) and CO_2 concentrations. Seasonal oscillations of atmospheric Hg(0) (red) and CO_2 (blue) concentration at seven monitoring sites around the globe. Fine lines represent daily and bold lines represent monthly anomalies normalized for long-term linear trends. All data meeting QA/QC criteria of the respective site are presented.

Fig. 2: Effect of latitude on Hg(0) seasonality A: Interhemispherical Gradient of Hg(0) at background sites (<2 ng/m^3) for February and September. **B:** Seasonal amplitude of Hg(0) (September mean - February mean) as a function of latitude for coastal (squares) and terrestrial (circles) sites. **C:** Seasonal amplitudes of Hg(0) (Sep-Feb) and CO_2 (Aug-Feb) variation measured at 7 atmospheric sites. The error bars represent the interannual variability (1σ). The lines represents the linear regression of the data and the shaded area the 95% confidence area of the regression.

Figure 3: Effect of vegetation activity on atmospheric Hg(0) and CO_2 concentration. Linear regression between multi-year averages of monthly Hg(0) concentration (left) or CO_2 concentration (right) and vegetation activity (NDVI). lines represents the linear regression of the data and the shaded area the 95% confidence area of the regression.

Fig. 4: Seasonal variation of Hg emission, vegetation activity and atmospheric Hg(0) concentration. Seasonal variation of Hg emissions in gray, atmospheric Hg(0) concentration at terrestrial background sites (Hg(0) Bg) in blue and at urban sites (Hg(0) urban) in red and vegetation activity (NDVI) in green. Monthly Hg emission and Hg(0) concentrations are reported relative to yearly average. The bold lines represent averages and the shaded areas represent 25th to 75th percentiles.

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AUTHOR CONTRIBUTIONS:
MJ initiated the project, performed the data analysis and wrote the manuscript together with JES and contributions from DO, JB and AD. JB, RE, CML, KAP, IW, KK, DW, LM, CL, TM, MR, OM, and AD provided data. All Authors read and commented on the manuscript.

METHODS:

Atmospheric CO_2 and Hg(0) measurements. The focus of the present analysis is on atmospheric monitoring sites that simultaneously measured Hg(0) and CO_2 concentrations. As atmospheric oxidized mercury species account for a minor fraction of total atmospheric Hg (Hg_{tot}) in the PBL, no difference was made between Hg(0) and Hg_{tot} and all data are reported as Hg(0). High resolution QA/QC controlled Hg(0) and CO_2 data were obtained from global air monitoring databases or directly from the responsible site scientists. The European data are harmonised and quality assured following the EMEP program and monitoring strategy.[52] Hg(0) concentrations at all sites except Pallas were measured at high frequency (5-15 min) using Tekran Continous Mercury Vapor Analyzers 2537 and reported as 1h averages. For Cape Point, SA and Amsterdam Island, Fr all Hg(0) measurements were made in compliance with the GMOS quality assurance protocol (www.gmos.eu). Hg(0) concentrations at Pallas were measured using a semi-automatic sampling on Au-traps (quartz glass coated with gold) at an air sampling rate of 300 ml/min during 24h periods, two days per week. The samples were analyzed on a Tekran 2500 CVAFS Mercury Detector at the IVL laboratory in Gothenburg. CO_2 at Birkenes was measured with Cavity Ringdown spectroscopy (CRDS), Picarro G1301 with 5 s resolution, average to 1 h if data coverage was more than 75%. The data are calibrated against WMO- Global Atmospheric Watch standards at EMPA. CO_2 data from Amsterdam Island, Fr was measured using CRDS and from Egbert, Ca and Cape Point, SA using Non-Dispersive Infrared (NDIR) sensors. CO_2 data from Schauinsland, De were measured by IR-Absorption. All data from Birkenes, No, Amsterdam Island, Fr, Egbert, Ca, Cape Point, SA and Schauinsland, De were measured continuously and reported as hourly averages. CO_2 data from Pallas, Fi and Mace Head, Ir were measured on an event base with flasks and analysed using NDIR.[53] Monthly average Hg(0) data were obtained from.[4,6,43,44,54-61]

Normal Differenced Vegetation Index, (NDVI) were obtained from the NASA Earth Observations (NEO) platform at 16 days and 0.1° resolution. NDVI data are derived from Moderate Resolution Imaging Spectroradiometer (MODIS) images aboard the NASA's Terra and Aqua satellites.

Statistics

Long-term trends of time series as well as linear regression's were calculated with the *lm* function and confidence intervals with the *confint* and *predict* functions of R.[62] Students t-tests were performed with Microsoft Excel assuming uneven variances.

Seasonality of anthropogenic Hg emission. The monthly Hg emission for the different regions ($F(Hg)_{month}$) in Mg Hg/month was calculated according to Formula 1:

$$F(Hg)_{month} = f_{coal} * f_{consumption} * FHg_{year} + (1 - f_{coal}) * {}^{1}/_{12} * FHg_{year} \quad (1)$$

where f_{coal} and $F(Hg)_{year}$ corresponds to the fraction of Hg emission based on coal combustion and the total yearly Hg emission for each investigated country, based on the AMAP/UNEP 2010 mercury emission estimates.[32] $f_{consumption}$ corresponds to the monthly fraction of the yearly coal consumption. For the USA and Europe (27 EU countries) monthly coal consumption data are reported by governmental agencies. Seasonality of Hg emission from China was derived from the monthly power generation data between 2005 and 2010 reported by Liu et al. 2015.[63] The monthly cement production in China was considered constant throughout the year.[64]

Normalization of monthly Hg concentration and emission data. In Figure 1 monthly Hg concentrations and emission fluxes are normalized to yearly averages for comparability. Hg concentrations are normalized as follows: $C(Hg0)_{monthx}/C(Hg0)_{year}$, were $C(Hg0)_{monthx}$ represents the multiyear monthly average of month x and $C(Hg0)_{year}$ the yearly average.

Computation of Seasonal Amplitudes. The absolute seasonal amplitudes are calculated from the multiyear monthly averages as follows: (μM_{max} - μM_{min}), were μM_{max} and μM_{min} represent the averages of the months with NH maximum (February for both Hg(0) and CO_2) and minimum (August for CO_2 and September for Hg(0)) concentration (Table S6-S10), respectively. Relative amplitudes are calculated as follows: (μM_{max} - μM_{min})/ μY, were μY represents the yearly average.

DATA SOURCES AND AVAILABILITY:

Most European Hg(0) data used are associated to EMEP, and publically available through the EMEP data base, EBAS: http://ebas.nilu.no. CO_2 concentrations were obtained from the ESRL NOAA Global Monitoring Division database (ftp://aftp.cmdl.noaa.gov/data/trace_gases/co2/flask/surface/co2_mhd_surface-flask_1_ccgg_event.txt, ftp://aftp.cmdl.noaa.gov/data/trace_gases/co2/flask/surface/co2_pal_surface-flask_1_ccgg_event.txt) and the World Data Center for Greenhouse Gases WDCGG (http://ds.data.jma.go.jp/gmd/wdcgg/). Canadian Hg(0) concentrations were obtained from the National Atmospheric Chemistry (NAtChem) Database and Analysis Facility of Environment Canada (www.ec.gc.ca/natchem).

For the USA and Europe (27 EU countries) monthly coal consumption are reported by the U.S. Energy Information Administration (http://www.eia.gov/totalenergy, downloaded 25.5.2016) and Eurostat (http://ec.europa.eu/eurostat/statistics-explained/index.php/Coal_consumption_statistics, downloaded 15.2.2016), respectively.

NDVI data was obtained from the NASA Earth Observations (NEO) platform (http://neo.sci.gsfc.nasa.gov)

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